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(54) Radiation curable polyolefin pressure-sensitive adhesive.

(57) Pressure sensitive adhesive compositions comprise one or more poly(alpha-olefin) homopolymers, copolymers, terpolymers, and tetrapolymers derived from monomers containing 6 to 10 carbon atoms and photoactive crosslinking agents. Radiation curing provides adhesive films having a superior balance of peel and shear adhesive properties. The pressure sensitive adhesive is useful in pressure sensitive adhesive tapes, in articles containing transfer adhesive films, and as the bonding material between supports in a laminated structure.

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RADIATION CURABLE POLYOLEFIN PRESSURE SENSITIVE ADHESIVE

FIELD OF THE INVENTION

5 The invention relates to radiation curable poly(α -olefin) pressure-sensitive adhesive compositions having superior cohesive strength and shear adhesion and to laminated structures made therefrom which are useful as high temperature tapes and transfer adhesives.

BACKGROUND OF THE INVENTION

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A continuing need in the pressure-sensitive adhesive (PSA) art is achievement of better control over various mechanical and process properties so that adhesives can be "tailor-made" for specific, highly demanding end-use applications such as packaging, medical, and masking tapes. These applications
15 require a proper balance of properties, and this balance changes with the particular end-use.

Among the earliest polymers to provide a reasonable balance of the properties required for satisfactory PSA performance were the natural and synthetic rubbers. However, these PSAs had poor aging properties, and the art quickly recognized the need to eliminate ethylenically unsaturated groups from the polymer backbone of rubber adhesives in order to improve their oxidative stability.

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This became possible with the discovery of Ziegler-Natta (ZN) coordination catalyst systems. With the discovery of ZN catalysts, it became possible to polymerize α -olefin monomers to high molecular weight. The homopolymers of the C_6 - C_{10} α -olefins were naturally tacky and therefore good candidates for PSAs since they also had low toxicity, good aging and favorable environmental stability (i.e., low oxidation). These homopolymers were chemically inert, resistant to plasticizer migration, and relatively inexpensive. However
25 they had poor cohesive strength and therefore lacked the shear adhesion necessary for high performance PSAs.

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Use of ZN catalysts to make homopolymers from α -olefin monomers, and copolymers from mixtures of α -olefin and non-conjugated polyene monomers is old in the art and is not the subject of this invention. ZN polymerizations are succinctly summarized in Odian, G., "Principles of Polymerization", Ch. 8.4 (Second Edition, J. Wiley & Sons, New York, 1981). For a more detailed discussion of the polymerization of α -olefins, see Boor, J., "Ziegler-Natta Catalysts and Polymerizations", Ch. 19 (Academic Press, NY, 1979).

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Radiation curing has been frequently used to chemically crosslink the polymeric component of adhesives in attempts to increase the cohesive strength of coated adhesive films. The results have been unsatisfactory because competing crosslinking and degradation (chain scission) reactions occur simultaneously. Therefore in some PSA systems, especially those formulated from polymers containing propylene,
36 radiation curing leads to a loss of cohesive strength and shear adhesion.

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Adhesives derived primarily from C_6 or larger α -olefins are well known in the art. U.S. Patent No. 3,542,717 describes poly(α -olefin) adhesive compositions comprising mixtures of polyolefin copolymers derived from olefin monomers with different molecular weights. (i.e. α -olefins having 11-20 carbon atoms, and different α -olefins having 4-20 carbon atoms.) The resulting adhesive has high shear and peel adhesion at room temperature, but at high temperatures cohesive strength and shear adhesion are unacceptably low for most applications.

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U.S. Patent 3,635,755 describes PSA polyolefin compounds suitable for use as single component PSAs for surgical tapes that are substantially non-allergenic. Such adhesives can be made from homopolymers of the C_6 to C_{11} α -olefins or from interpolymers of C_2 to C_{16} α -olefins having an intrinsic viscosity of 1.5 to 7.0, a Williams' plasticity of 0.8 to 4.0, and an acetone/heptane soluble fraction of less than 25% by weight.

Tapes made from these adhesives have low shear adhesions that facilitate non-irritating removal from the skin. However, this low shear adhesion is unsuitable, for example, for masking or packaging tape applications.

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U.S. Patent Nos. 3,954,697 and 4,178,272 describe hot-melt adhesives derived from copolymers of propylene and C_6 - C_{10} α -olefins. The '697 patent teaches that while C_6 - C_{10} α -olefin homopolymers are permanently tacky, they have poor cohesive strength and consequently lack shear adhesion. Therefore the higher α -olefins must be copolymerized with propylene in order to meet "the critical property requirements for a pressure-sensitive adhesive material" (col. 1, line 37). The copolymer must contain more than 40 mole % propylene, especially if static shear is to exceed 1000 minutes. The '272 patent describes compositions

of ZN catalyst system and process conditions useful in preparing the "tacky" copolymers required for PSAs. Also disclosed are stereo-regulating three-component ZN catalyst systems that produce high molecular weight, crystalline block copolymers unsuitable for PSA applications (col. 2, lines 39-65), but are stated to be useful in preparing the sulfur vulcanizates hereinafter described.

5 This approach is further advanced in U.S. Patent No. 4,288,358 which describes hot-melt adhesive compositions containing terpolymers of propylene, 1-butene/1-pentene, and C₆-C₁₀ α -olefins; tackifying resins; and plasticizing oils, in yet further efforts to simultaneously optimize the adhesive and process properties of these compositions.

10 While these references teach optimized processing conditions for preparation of hot melt adhesives that are readily coatable or extrudable at the melt temperature, these materials have poor PSA properties. In particular, they have poor adhesion under shear. To be useful, high temperature masking tapes used in the automotive industry must have good "shear adhesion". Attempts to improve these propylene containing poly(α -olefin) adhesives of the references by radiation crosslinking have led to a degradation of PSA properties, such as shear adhesion.

15 U.S. Patent No. 2,933,480 describes two-component coordination catalyst systems (ZN) capable of copolymerizing mixtures of α -olefins and non-conjugated diolefins to yield sulfur-vulcanizable elastomers described as "rubber-like" with iodine numbers of 3 to 50, and intrinsic viscosities of 0.5 to 5.0.

20 U.S. Patent Nos. 4,340,705 and 4,551,503 describe 3-component ZN catalyst systems for the copolymerization of mixtures of α -olefins and non-conjugated α,ω -diolefins to yield sulfur vulcanizates having high molecular weight, high inherent viscosity (5 or greater), low gel (0-5 %), and improved (higher) unsaturation which provide improved vulcanizate properties.

No utility as adhesives is taught or claimed for the vulcanizates described in any of the three patents referenced above.

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SUMMARY OF THE INVENTION

30 Briefly, the present invention provides a radiation curable poly(α -olefin)-containing adhesive composition that is pressure-sensitive at room temperatures and which upon cure yields an adhesive film having a superior balance of peel and shear adhesion and comprising:

a) at least one polymer comprised of: 85 to 100 mole percent, preferably 85 to 99 mole percent, of one or more C₆ to C₁₀ α -olefin monomers, and 15 to 0 mole percent, preferably 15 to 1.0 mole percent, of one or more polyene monomers, with the proviso that the mole percentages of all monomers sum to 100; and

35 b) sufficient photoactive crosslinking agent to crosslink the composition upon irradiation from a source of actinic radiation. Preferably the polymer of the present invention has a glass transition temperature (T_g) in the range of -70°C to 0°C, more preferably in the range of -60 to -20°C, an inherent viscosity in the range of 0.4 to 9.0 dl/g, more preferably 0.5 to 6.0 dl/g, and most preferably 1.5 to 4.0 dl/g. Number average molecular weights of the polymers are in the range of 5,000 to 50,000,000, preferably 50,000 to 5,000,000.

40 Polymers formed from polyene monomers contain residual ethylenically unsaturated groups in the polymer backbone and/or, preferably, in pendant side chains that can be used in radiation initiated crosslinking reactions to improve the cohesive strength of the adhesive.

45 Compositions with improved PSA properties may be made by blending two or more polymers of the invention or by blending polymers and tackifying resins. Such compositions are obtained by blending 100 parts by weight of the polymer with from more than zero and preferably in the range of 1 to 150 parts by weight of a tackifying resin.

50 Poly(α -olefins) have excellent adhesion, thermal-oxidative stability, and chemical/electrical resistance, and they are physiologically inert. These properties make them excellent pressure-sensitive adhesives for a wide range of applications where it is desirable to have independent control of peel and shear adhesion.

It is believed that the background art does not teach PSA compositions comprising one or more poly(α -olefin) homopolymers, copolymers, terpolymers, or tetrapolymers derived from monomers containing 6 to 10 carbon atoms and further comprising one or more photoactive crosslinking agents, the compositions 55 having been radiation-cured to yield adhesive films possessing substantial high temperature shear strength.

The present invention provides a poly(α -olefin)-containing adhesive composition that is radiation-curable. The poly(α -olefin) adhesive composition can be cured to yield a PSA adhesive film with an improved balance of peel and shear adhesion. The peel and shear adhesion values are capable of being

varied independently to achieve desired values. Adhesive films of the invention preferably have peel values in the range of 2 to 120 N/dm and shear values in the range of 1 to 10,000 or more minutes. Radiation curing can be achieved by ultraviolet or electron beam radiation.

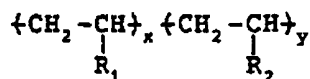
The adhesive of the invention can be applied to appropriate substrate surfaces by a wide range of processes, i.e., solution coating, solution spraying, hot-melt extrusion, emulsion coating, etc., to make adhesive tapes, adhesive transfer films, and the like.

As used in this invention:

"polymer" means a homopolymer, a copolymer, a terpolymer, or a tetrapolymer; polymers derived from more than one monomer may be either random or block polymers; "polyene monomer" means a C₄-C₂₄ hydrocarbon containing two or more conjugated or non-conjugated ethylenically unsaturated groups which may also contain 1 to 5 unitary heteroatoms selected from the group consisting of oxygen and silicon; "photoactive crosslinking agent" means a compound which, under the influence of radiation, connects polymer chains and becomes incorporated therein; this increases the molecular weight of the adhesive and thus its cohesive strength without unduly affecting its compliance or other PSA properties.

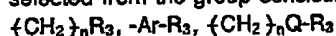
DESCRIPTION OF PREFERRED EMBODIMENTS

The radiation-curable α -olefin polymers of the invention preferably have the general formula:



where R₁ can be selected from monovalent hydrocarbon groups containing 4 - 8 carbon atoms. Representative examples include, but are not limited to: n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl; and branched hydrocarbon radicals such as 2-methyl-butyl, 2-ethyl-butyl, 3-methyl-hexyl, 2-ethyl-hexyl, 5-methyl-hexyl, 5-ethyl-hexyl, etc.

R₂ can be a monovalent hydrocarbon group containing one or more ethylenically unsaturated groups selected from the group consisting of:

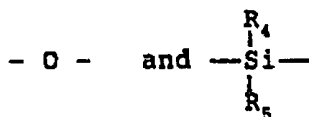


n = 0-14;

R₃ can be a C₂ to C₁₀ monovalent hydrocarbon group containing one or more ethylenically unsaturated groups;

Ar can be a divalent aromatic radical containing 1 or 2 fused or catenated aromatic rings with from 0 - 8 substituents selected from the group consisting of alkyl, aryl, cycloalkyl, alkoxy, and aryloxy containing from 1 - 12 carbon atoms;

Q can be a divalent group selected from the group consisting of



where R₄ and R₅ are the same or different C₁ to C₁₀ monovalent organic groups selected from the group consisting of alkyl, cycloalkyl, alkaryl, aryl, alkoxy, aryloxy;

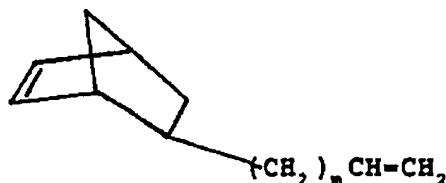
x is the mole percent of one or more C₆ - C₁₀ α -olefin monomer(s), the total ranging from 85 - 100 mole percent;

preferably y is the mole percent of one or more polyene monomer(s), the total ranging from 15 - 0 mole percent;

with the proviso that x + y = 100 mole percent.

The preferred ratio of x:y is about 85:15, and more preferably 90:10 when the pendant unsaturation is an internal olefin, and most preferably 95:5 when the pendant unsaturation is a terminal olefin as in the case of the linear alpha,omega-dienes.

Suitable polyene monomers useful in the practice of the present invention are comprised of hydrocarbons containing two to four ethylenically unsaturated groups. Examples of suitable polyenes, many of which are commercially available, include, but are not limited to: the C_6 - C_{14} alpha,omega dienes such as 1,5-hexadiene, 1,8-heptadiene and 1,9-decadiene; conjugated dienes such as 2-phenyl-1,3-butadiene, 2,3-diphenyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 2-isopropyl-1,3-butadiene, 2-n-amy-1,3-butadiene, 2,3-dibutyl-1,3-butadiene, isoprene, 1,3-pentadiene, and cyclooctadiene; trienes such as 1,4,7-octatriene, 1,4,9-decatriene, 1,5,9-decatriene, 1,6,8-decatriene, 1,9,12-octadecatriene, 1,9,17-octadecatriene, 2,6-dimethyl-2,4,6-octatriene (alloocimene), and cyclododecatriene; terpenes such as myrcene and farnesene; mono/multi-cyclic dienes, such as 4-vinyl-1-cyclohexene, 5-ethylidene-2-norbornene, dicyclopentadiene, limonene, beta-pinene, methylene-norbornene and various alkenyl-norbornenes with the structure:



where m is an integer from 1 to 18.

2-ethyl-1,3-butadiene and 2-isopropyl-1,3-butadiene can be prepared according to the method of Marvel et al., JACS, 70, 1948, p. 1894. 2-n-amy-1,3-butadiene can be prepared according to the method of Marvel & Williams, JACS, 70, 1948, p. 3842. The general synthetic route to make various 2-alkyl-1,2-butadienes has been described in Encyclopedia of Polymer Science & Technology Vol. 2, pp. 515-518 (1988). 1,9,17-octadecatriene can be prepared according to the method of Marvel & Rodgers, J. of Polymer Sci., XLIX, 1961, p. 335.

The poly(α -olefin) polymers of the present invention can be either random co, ter, or tetra polymers; or blocks of homopoly(α -olefins) interspersed with polyene units depending upon the relative reactivities of the various monomers. Since the reactivity at each end of the alpha,omega dienes are about equal, gel-permeation chromatographic analysis (with low-angle light scattering detector) of polymers containing these monomers show more branching than observed with monomers having double bonds of unequal reactivity. When diene monomers in which the reactivities of the double bonds are unequal are polymerized, as is the case with 7-octenyl-dimethylvinylsilane, essentially linear polymers are formed during ZN polymerization.

The polyene monomers are selected from the group consisting of aliphatic dienes, aliphatic trienes, aliphatic tetraenes, aromatic dienes, aromatic trienes, aromatic tetraenes, monocyclic dienes, bicyclic dienes, tricyclic dienes, tetracyclic dienes, monocyclic trienes, bicyclic trienes, tricyclic trienes, and tetracyclic trienes.

The α -olefin and polyene monomers can be polymerized in the presence of Ziegler-Natta (ZN) catalysts over a wide range of temperatures, e.g., 0 to 140°C, preferably 30 to 90°C. The polymerization can be done in bulk or in inert solvents. Suitable examples of inert solvents include, but are not limited to, the aliphatic, aromatic, and cycloaliphatic hydrocarbon solvents, i.e., hexane, heptane, benzene, toluene, cyclopentane, and cyclohexane. The amount of catalyst used is preferably in the range of 0.1 g to 5 g per Kg of monomer, more preferably 0.2 to 5 g per Kg of monomer, and most preferably 0.5 to 2 g per Kg of monomer. ZN catalysts are well known in the art and are disclosed, for example, in Odian, G., *supra*, and Boor, J., *supra*.

NMR analysis of the polymers shows the presence of ethylenic unsaturation only in the pendant side-chains when the polyene monomers are non-conjugated alpha, omega-dienes. For conjugated diene monomers, e.g., isoprene or 1,3-butadiene, or for certain triene monomers, e.g., myrcene, the unsaturation appears in both the backbone and the pendant side-chains. This occurs because the polymerization proceeds by both a 1,2 and a 1,4 polymerization mechanism (ref. Odian [*supra*] pp. 297-298). The 1,2 polymerization yields unsaturation in the pendant side-chains and the 1,4 polymerization yields unsaturation in the polymer backbone.

Radiation curable terpolymers have been made by polymerizing mixtures of two different C_6 to C_{10} α -olefins and a single polyene. Tetrapolymers have been made by polymerizing mixtures of two different C_6 to C_{10} α -olefins, a diene with double bonds of equal reactivity, and a diene with double bonds of unequal reactivity. The branched structure and unhindered ethylenic unsaturation in such tetrapolymers facilitates the coating and radiation curing processes used to form crosslinked PSA films from the compositions of this

invention. Blends of two or more of these polymers in any proportion, e.g., ratios in the range of 0.1:9.9 to 9.9:0.1, preferably 1:9 to 9:1, can also be used to formulate compositions that yield PSA films with the peel and shear adhesion properties required for various specialized end-use applications.

Such PSA films which are free of sulfur can be prepared by activating such an adhesive composition, which contains a photocrosslinking agent, by actinic radiation. Suitable photocrosslinking agents include, but are not limited to: aldehydes, such as benzaldehyde, acetaldehyde, and their substituted derivatives; ketones such as acetophenone, benzophenone and their substituted derivatives such as Sandoray 1000TM - (Sandoz Chemicals, Inc., Charlotte, NC); quinones such as the benzoquinones, anthraquinone and their substituted derivatives; thioxanthenes such as 2-isopropylthioxanthone and 2-dodecylthioxanthone; and certain chromophore-substituted vinyl halomethyl-sym-triazines such as 2,4-bis-(trichloromethyl)-6-(3',4'-dimethoxyphenyl)-sym-triazine. The concentration of photoactive crosslinking agent can be present in the range of 0.05 to 6.0, preferably 0.1 to 2 percent by weight of the polymer, and more preferably 0.5 to 1.5 percent by weight.

The adhesive composition of the present invention can be coated from solution by any of coating processes well known in the art, such as knife coating, roll coating, gravure coating, curtain coating, etc. Useful coating thicknesses for the present invention are in the range of 0.5 to 15 mg/cm², preferably in the range of 2.0 to 7.0 mg/cm². Furthermore, some of the compositions of the invention can be applied by extrusion coating with no solvent present thereby eliminating environmental and toxicity problems associated with solution coating processes.

The adhesive composition can be cured using a source of actinic radiation of sufficient energy (i.e., wavelength range) to generate free radicals when incident upon the particular photoactive crosslinking agent selected for use in the composition. The preferable wavelength range for the photoactive crosslinking agents disclosed above is 400 to 250 nm. The radiant energy in this preferred range of wavelengths required to crosslink the adhesive film of the invention is 100 to 1500 millijoules/cm² and more preferably 200 to 800 millijoules/cm². Details of the photocure process are disclosed in U.S. Patent Nos. 4,181,752 and 4,329,384. Since the adhesive composition of the present invention contains a polymer, the pre-polymerization (making of a syrup) step disclosed in the '752 and '384 patents is not required and is omitted in photocuring the composition of the present invention.

The adhesive composition, without any crosslinking agent present, can also be cured using electron beam (E-beam) radiation. The preferred dosage required to crosslink the adhesive film of the invention is from 1 to 20 megarads (Mrads), preferably from 2 to 10 Mrads. Details of suitable process for E-beam curing substrates that have been coated with adhesive composition of the invention can be found in U.S. Patent No. 4,533,566, which is hereby incorporated for reference.

The crosslinked adhesive films preferably have a percent gel in the range of from 2 to 85 weight percent, more preferably from 30 to 80 weight percent, and most preferably from 50 to 70 weight percent when the percent gel has been corrected for soluble tackifying resins and other additives as hereinafter described.

The addition of one or more tackifying resins to the inventive composition can provide a PSA having improved tack, lower viscosity, improved coatability, good heat stability, and improved peel adhesion. The shear adhesion of the tackified compositions can be enhanced by radiation cure with no loss of peel adhesion. The high internal strength of the adhesive is necessary in box sealing tapes and masking applications in the automotive industry.

Compatible tackifying resins useful in the radiation curable adhesive compositions of the invention include resins derived by polymerization from C₅ to C₉ unsaturated hydrocarbon monomers, polyterpenes, synthetic polyterpenes, and the like. Hydrocarbon tackifying resins can be prepared by polymerization of monomers consisting primarily of olefins and diolefins and include, for example, residual by-product monomers of the Isoprene manufacturing process. These hydrocarbon tackifying resins typically exhibit Ball and Ring Softening Points of from about 80°C to about 145°C; Acid Numbers of from about 0 to 2, and Saponification values of less than one. Examples of such commercially available resins based on a C₅ olefin fraction of this type are WingtackTM 95 and WingtackTM 115 (Wingtack Plus) tackifying resins available from Goodyear Tire and Rubber Co. Other hydrocarbon resins include RegalrezTM 1078 and RegalrezTM 1128 available from Hercules Chemical Co. Inc., Wilmington, DE; Arkon resins, such as ArkonTM P115, available from Arakawa Forest Chemical Industries, Chicago, IL; and EscorezTM resins available from Exxon Chemical Co.

Other suitable resins include the terpene polymers, such as polymeric resinous materials obtained by polymerization and/or copolymerization of terpene hydrocarbons such as the alicyclic, mono, and bicyclic monoterpenes and their mixtures, including carene, isomerized pinene, terpinene, terpenene, and various other terpenes. Commercially available resins of the terpene type include the ZonarezTM terpene B-series

and 7000 series available from the Arizona Chemical Corp., Wayne, NJ 07470. Typical properties reported for the ZonarezTM terpene resins include Ball and Ring Softening Points of about 55°C to 125°C (ASTM E28-67), Acid Numbers of less than one (ASTM D465-59), and Saponification Numbers of less than one (ASTM D464-59). The terpene resin used in examples below is a poly(beta-pinene) resin, PiccolyteTM A115 available from Hercules Chemical Co. Inc., which has a Ball and Ring Softening Point of 115°C, an Acid Number of one, and Iodine Number of 190.

The tackifying resins may contain ethylenic unsaturation; however, saturated tackifying resins are preferred for those applications where oxidation resistance is important. The total amount of tackifying resins in the composition is more than 0 to 150 parts, more preferably 5 to 50 parts, and most preferably 25 to 35 parts by weight per 100 parts of polymer. For poly(alpha-olefin) homopolymers, the saturated tackifying resins such as RegalrezTM 1078 and ArkonTM P115 are preferred because they yield a higher gel content upon equivalent treatment by an activated crosslinking agent.

Minor amounts of additives can also be included in the composition to provide adhesives for special end uses. Such additives may include pigments, dyes, plasticizers, fillers, stabilizers, ultraviolet absorbers, anti-oxidants, processing oils, and the like. Amount of additives used can vary from 0.1 to 50 weight percent depending on the end use desired.

The adhesive composition of the present invention can be coated onto a wide range of substrate materials, examples being polymer films such as polyethylene terephthalate (PET), and biaxially oriented polypropylene (BOPP); woven and non-woven fabrics; metals and metal foils such as aluminum, copper, lead, gold and the like; paper; glass; ceramics; and composite materials comprised of laminates of one or more of these materials.

Another embodiment of the invention comprises a laminated structure of at least a first and a second substrate, the substrates being joined by a layer of the adhesive composition of the invention. At least one of the substrates is capable of transmitting actinic or electron beam radiation so that the adhesive film may be cured.

In some applications primers may be useful for improving the adhesion of the adhesive to some substrates. Useful primers for the practice of the present invention include a triblock copolymer of styrene-ethylene/butylene-styrene grafted with maleic anhydride (KratonTM G-1901X, Shell Chemical Co.) and a combination of amorphous polypropylene and KratonTM G-1901X. Release liners (such as described in U.S. Patent Nos. 4,386,135, 3,957,724, and 2,532,011) form a special class of substrates on which the composition of the invention can be coated and subsequently radiation cured to form adhesive transfer films.

35 TEST METHODS :

The test procedures used in the examples to evaluate and compare the properties of the PSA compositions and tapes made from them are industry standard tests. These tests are described in detail in various publications of the American Society for Testing Materials (ASTM), Philadelphia, PA and the Pressure Sensitive Tape Council (PSTC), Glenview IL. References to these standards are also given.

Shear Strength (ASTM D-3854-78; PSTC - 7)

45 The shear strength is a measure of the cohesiveness or internal strength of an adhesive. It is based upon the amount of force required to pull an adhesive strip from a standard flat surface in a direction parallel to the surface to which it has been affixed with a definite pressure. It is measured in units of time (minutes) required to pull a standard area of PSA coated sheet material from a stainless steel test panel under stress of a constant, standard load.

50 The tests were conducted on adhesive coated strips applied to a stainless steel panel such that a 12.7 mm by 12.7 mm portion of each strip was in firm contact with the panel with one end portion of the tape being free. The panel with coated strip attached was held in a rack such that the coated surface of the panel forms an angle of 182° with the vertical tape free end which is then tensioned by application of a force of one kilogram applied as a hanging weight from the free end of the coated strip. The 2° greater than 180° is used to negate peel forces thus insuring that only the shear forces are measured in order to more accurately determine the holding power of the tape being tested. The time elapsed for each test specimen to separate from the steel panel is recorded as the shear strength.

Mode of Failure (MOF)

The time at which the mass falls is called "Shear Test" and is reported as "5000 + " if the tape has not failed after 5000 minutes. With each Shear is indicated the mode of failure as follows:

- 5 PP = pop-off, i.e., 75-100% adhesive failure from steelplate;
- Sp = adhesive split: both surfaces completely covered by adhesive;
- r = residue failure: adhesive covering 100% of backing with a small residue transferred to panel;
- SM = smear: adhesive covering 100% of backing with a substantial amount (less than 100%) transferred to panel;
- 10 FB = failure from backing: 75-100% adhesive failure from the backing; all adhesive adheres to panel.

The pop-off failure mode is preferred because it is indicative of adhesive failure of the adhesive/steel interfacial bond as opposed to cohesive failure of the adhesive. Adhesives of various shear adhesions, all within the range of the present invention (1 - 10,000 minutes), are preferred depending on end-use applications.

- 15 Two specimens of each tape were tested and the shear tests were averaged to obtain the shear value.

Peel Adhesion [ASTM D 3330-78; PSTC - 1 (11/75)]

- 20 The peel adhesion is the force required to remove a PSA coated test specimen from a test panel measured at a specific angle and rate of removal. In the examples, this force is expressed in Newtons per decimeter (N/dm) width of coated sheet. The procedure followed is:

- 1) A test specimen 12.7 mm wide is applied to a horizontally positioned clean glass test plate. A 2.2 kg rubber roller is used to press a 12.7 cm length of specimen into firm contact with the glass surface.
- 25 2) The free end of the specimen is doubled back nearly touching itself so the angle of removal is 180°. The free end is attached to the adhesion tester scale.
- 3) The glass test plate is clamped in the jaws of tensile testing machine which is capable of moving the plate away from the scale at a constant rate of 2.3 meters per minute.
- 4) The scale reading in Newtons is recorded as the tape is peeled from the glass surface.

30

Inherent Viscosity [ASTM D 2857-70 (Reapproved 1977)]

- 35 In order to understand the benefits derived from the teaching of this invention, it is necessary to relate the improvements in shear strength and processability to the molecular weight of the PSA. The inherent viscosity of 10 ml. of PSA solution is measured using a Cannon-Fenske #50 viscometer in a water bath controlled at 25° C. The solvent used is specified in the examples.

Percent Gel Test [ASTM D 3616-82]

- 40 The percent gel is used as an indication of cure level. The tapes containing tackifying resins are corrected to the actual percent gel. The corrected percent gel is 100 times the gelled mass divided by the total mass of material that is capable of forming a gelled network. Soluble materials such as tackifiers are
- 45 subtracted out when determining the gel fraction.

Crosslinking by radiation improves the creep and shear resistance of pressure-sensitive adhesives. The transition from a cohesive to an adhesive failure during peeling advances to a lower peel rate and higher temperature with increasing crosslinking density.

- Many important properties of crosslinked pressure-sensitive adhesives vary with the gel content. Hence,
- 50 determination of the gel content provides a means for controlling the process and thereby raising the quality of the tape.

Extraction tests permit verification of the proper gel content of polyolefin PSAs and they also permit comparison between different crosslinked adhesives and their specific end uses.

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Gel Content Determination :

A square test specimen (3.81 cm x 3.81 cm) containing approximately 0.06 g of PSA is cut from the

tape and placed in a 120-mesh stainless steel basket measuring approximately 4 x 8 cm. The contents are weighed to the nearest 0.1 mg and then immersed in a capped beaker containing sufficient toluene to cover the specimen. After extraction for 24 to 48 hours, the basket (containing the specimen) is removed, drained, and placed in an oven at 83°C. The basket and specimen are dried to a constant weight and the gel content is determined as follows:

$$\text{Extract \%} = \frac{\text{weight lost during extraction}}{\text{weight of original specimen}} \times 100$$

Gel content = 100 - percent extract

For the tackified pressure-sensitive adhesive tapes, the weight of the resin was subtracted before calculating the corrected gel content as follows:

$$\text{Percent extract (\%)} = \frac{\text{weight lost during extraction}}{\text{weight of final specimen} - \text{weight of resin}} \times 100$$

Corrected gel content = 100 - percent extract

Two specimens of each tape were tested and the results were averaged to obtain the gel content value.

EXAMPLES

A photocure process disclosed in U.S. Patent No. 4,181,752 can be used to practice the present invention. The laboratory scale coatings in the following examples were cured in nitrogen, in an RPC Processor Model #QC1202 ANIR (available from PPG Industries, Chicago, IL) at 30 cm/sec with two standard medium pressure mercury vapor lamps operating at 80 watts per centimeter. The lamps were located approximately 9.5 cm from the adhesive surface. Multiple passes through the processor were used to increase the degree of cure with no delay between subsequent passes. The number of passes is included in the examples.

The laboratory scale coatings described in the examples were cured using an ElectroCurtain Model CB150 (available from Energy Sciences, Inc., Woburn, MA) at a web speed of 1.4 m/min and an oxygen concentration of less than 100 ppm. The radiation dosage (Mrads) used to prepare the adhesives of the examples are included among the data.

Examples 1 to 65 pertain to the coordination polymerization of monomer mixtures to make copolymers useful in the practice of the present invention.

Examples 1 to 24 were made using vanadium/aluminum catalysts, while Examples 25 to 65 were made using titanium/aluminum catalysts.

Examples 66-145 pertain to ultraviolet radiation crosslinked PSA films that demonstrate the wide range of adhesive properties obtainable using the invention. Examples 66-99 pertain to non-tackified adhesive films. Examples 100-145 pertain to tackified adhesives.

Examples 146-219 pertain to E-beam crosslinked PSA films that demonstrate the wide-range of adhesive properties obtainable using the invention. Examples 146-181 pertain to non-tackified adhesive films. Examples 182-219 pertain to tackified adhesives.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions, and details, should not be construed to unduly limit this invention.

Example 1 - Synthesis of 1-hexene/1,7-octadiene copolymer (weight ratio 98:2) using a vanadium catalyst.

The following reactants were charged in the order named to a dry, argon filled, circulating water jacketed glass reactor equipped with stirrer and dry ice condenser: 625 g dry heptane, 490 g of 1-hexene (Gulfene-6TM, available from Gulf Oil) which had been passed through alumina/silica to remove impurities

and then dried over molecular sieves), 10 gm 1,7-octadiene, and 4.89 g (0.03 mole) VCl_3 . The copolymerization was initiated by the slow addition of 8.2 ml (0.015 mole) of $(\text{C}_2\text{H}_5)_3\text{Al}$ 1.9M in toluene. The copolymerization was exothermic, and the reaction mixture was cooled by circulating water through the reactor jacket to maintain the temperature at 25°C for five hours. One liter of methanol was added to deactivate the catalyst. The methanol was decanted from the copolymer and the soft, sticky, light green colored copolymer was washed with additional methanol to remove the catalyst residues. The copolymer was stabilized with 0.25 weight percent IRGANOXTM 1010 (a hindered phenol antioxidant available from Ciba-Geigy), and vacuum stripped at 100°C . The yield of copolymer was 85 weight percent.

The tacky copolymer had a glass transition temperature, T_g , of -42°C as measured by Differential Scanning Calorimetry (DSC) analysis. It contained about 1.8 mole percent unsaturation as determined by NMR analysis.

Examples 2-24

Using the procedure, catalysts, and concentrations of Example 1, the following monomers were polymerized. The results are shown in Table I.

TABLE I

5	Ex. #	Monomers ^(a) and Molar Ratios	Polymer	T _g ^(b)
			Yield (%)	(°C)
	2	100 H	96	-42
10	3	99 H : 1 OD	92	-41
	4	98 H : 2 OD	79	ND ^(c)
	5	95 H : 5 OD	58	-40
15	6	99 H : 1 VCH	85	-42
	7	98 H : 2 VCH	79	-42
	8	95 H : 5 VCH	67	-44
20	9	90 H : 10 VCH	61	ND
	10	99 H : 1 ENB	65	ND
	11	98 H : 2 ENB	58	ND
	12	95 H : 5 ENB	56	ND
25	13	90 H : 10 ENB	45	ND
30	14	100 O	98	-61
	15	99 O : 1 VCH	87	ND
	16	98 O : 2 VCH	89	ND
	17	97 O : 3 VCH	76	ND
	18	96 O : 4 VCH	82	ND
35	19	95 O : 5 VCH	75	ND
	20	90 O : 10 VCH	62	ND
40	21	98 O : 2 ENB	68	ND
	22	95 O : 5 ENB	59	ND
	23	90 O : 10 ENB	57	ND
45	24	50 O : 45 H : 5 OD	85	-52
50				
55				

TABLE I (continued)

5	(a) H	=	1-hexene
	O	=	1-octene
	OD	=	1,7-octadiene
	VCH	=	4-vinylcyclohex-1-ene
10	ENB	=	5-ethylidene-2-norbornene
	(c) ND	=	not determined
	(b) T _g	=	glass transition temperature

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Example 25 - Synthesis of 1-octene/VCH copolymers using a titanium catalyst

20 The following reactants were charged to reactor of Example 1 in the order named: 200 g of heptane, 200 g of 1-octene (dried over molecular sieves), 4 g of VCH, and 0.08 g of supported aluminum-activated reduced TiCl₃ (AATiCl₃TM) catalyst (available from Stauffer Chemical Co., Inc.). The copolymerization was initiated by the slow addition of 0.28 ml of 1.9 M (C₂H₅)₃Al which provided a molar ratio (C₂H₅)₃Al/AATiCl₃ of 2.5/1.0. The reaction mixture was maintained at 25 °C for 7.5 hours. The resulting copolymer was isolated
 25 by precipitation in excess methanol (85 weight percent conversion). It had a T_g of -59 °C and an inherent viscosity of 4.5 dl/g in hexane solution.

Example 26

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The procedure of Example 25 was used to copolymerize 1-octene/1,7-octadiene in a weight ratio of 95:5. In this example, the polymerization was performed in dry toluene at 50 weight percent monomer. The yield was 65 percent after 18 hours of polymerization. The polymer had a T_g of -58 °C, and an inherent viscosity of 4.7 dl/g in hexane solution.

35 When the polymerization temperature was raised to 90 °C the polymerization yield was 72 percent by weight after 10 hours of polymerization. This polymer had a T_g of -58 °C and an inherent viscosity of 2.2 dl/g in hexane solution.

Example 27

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The procedure of Example 26 was used to copolymerize 1-octene/1,7-octadiene in a weight ratio 90/10. The yield was 81 percent. The polymer had a T_g of -57 °C, an inherent viscosity of 5.5 dl/g in hexane solution and gel content of 12% weight.

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Example 28

The polymerization of Example 26 was repeated at a temperature of 90 °C for 5 hours. The copolymer
 50 was precipitated in methanol (79 weight percent conversion) and stabilized against oxidation by the addition of 0.25% by weight IRGANOX 1010. This copolymer had a T_g of -59 °C and an inherent viscosity of 1.9 dl/g in hexane solution.

Examples 29-65

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Using the procedure, catalysts, and concentrations specified in Example 28 a number of polymerizations were performed with the weight ratios of 1-Hexene (H) or 1-Octene (O) and the polyene co-monomers

Indicated in Table II.

TABLE II

Ex. #	Monomers ^(a) and Wt. Ratios	Polymer Yield (%)	IV ^(d) (dl/g)	T _g (°C)
29	99 H : 1 OD	85	5.5	-41
30	95 H : 5 OD	72	4.7	-40
31	90 H : 10 OD	56	3.9	-36
32	99 H : 1 VCH	87	5.2	-42

TABLE II (continued)

Ex. #	Monomers ^(a) and Wt. Ratios	Polymer Yield (%)	IV ^(d) (dl/g)	T _g (°C)
33	98 H : 2 VCH	65	4.6	-42
34	95 H : 5 VCH	61	3.7	-44
35	90 H : 10 VCH	65	3.8	-41
36	98 H : 2 ENB	69	4.5	-42
37	95 H : 5 ENB	45	3.9	-42
38	90 H : 10 ENB	37	3.2	ND ^(c)
39	99 O : 1 VCH	72	4.7	ND
40	98 O : 2 VCH	71	4.8	-62
41	97 O : 3 VCH	67	4.9	-64
42	96 O : 4 VCH	72	ND	-64
43	95 O : 5 VCH	63	ND	-68
44	90 O : 10 VCH	57	3.6	-71
45	98 O : 2 ENB	62	ND	-63
46	95 O : 5 ENB	56	ND	-65
47	90 O : 10 ENB	45	ND	-62
48	97 O : 3 myrcene	52	ND	-62
49	90 O : 10 myrcene	47	ND	-66
50	90 O : 10 beta-pinene	56	ND	-66
51	85 O : 15 beta-pinene	43	ND	-71
52	90 O : 10 limonene	37	ND	-65
53	90 O : 10 styrene	62	5.7	-68
54	90 O : 10 isoprene	57	ND	-69
55	99 O : 1 benzophenone acrylate	22	ND	-63

TABLE II (continued)

Ex. #	Monomers ^(a)	and Wt. Ratios	Polymer Yield (%)	IV ^(d) (dl/g)	T _g (°C)
56	100	1-heptene	56	2.0	ND ^(c)
57	95	1-heptene : 5 VCH	32	3.2	ND
58	100	1-nonene	46	4.1	ND
59	95	1-nonene : 5 VCH	37	2.7	ND
60	100	1-decene	95	6.2	-64
61	90	1-decene : 10 BP	60	ND	-71
62	50 O : 45 H : 5 OD		75	ND	-50
63	50 O : 47 H : 3 OD		78	ND	-52
64	50 O : 48 H : 2 OD		82	ND	-53
65	50 O : 49 H : 1 OD		91	ND	-53

^(a) H = 1-hexene

O = 1-octene

OD = 1,7-octadiene

VCH = 4-vinylcyclohex-1-ene

ENB = 5-ethylidene-2-norbornene

BP = beta-pinene

^(d) IV = inherent viscosity at 0.2 gm/dl concentration

^(c) ND = not determined

Examples 86-99 - UV Cured Non-tackified Adhesive Tapes

Adhesive solutions of the indicated copolymers in toluene solvent (polymers were prepared according to the general procedure of Example 25) were knife coated on a 25 micrometer (μm) PET backing (3M) using a handsread coater (dry coating weights were 3.8 mg/sq. cm). The handsreads were dried at 80 °C for 5 min to remove toluene. The handsreads were cured in nitrogen in an RPCTM Processor Model #QC1202 ANIR (from PPG Industries) at 30 cm/sec (60 ft/min) with two standard medium pressure mercury lamps operating at 80 watts per centimeter. The lamps were located at a distance of about 8.5 cm from the backing. Different types of photoinitiators were used. The results for these photocured tapes are shown in Table III.

TABLE III

Ex. #	Monomers ^(a) (wt. ratio)	Photoinitiator ^(e) (Conc.)(Wt.%)	No. Passes	Peel Adh. (N/dm)	Shear (Min.)	MOF ^(f)	Gel (%)
66	100 hexene-1	0	0	29	1	SP	0
67	100 hexene-1	ITX (1.0)	2	24	30	r	74
68	98H-20D	0	0	49	5	SP	3
69	98H-20D	ITX (1.0)	4	45	49	PP	81
70	95H-50D	0	0	31	3	SP	12
71	95H-50D	ITX (0.5)	4	27	49	PP	89
72	98H-2VCH	0	0	30	10	SP	2
73	98H-2VCH	ITX (1.0)	2	27	35	PP	75
74	95H-5VCH	0	0	26	13	SP	0
75	95H-5VCH	ITX (1.0)	2	22	5000+		88
76	95H-5ENB	0	0	28	20	SP	0
77	95H-5ENB	ITX (1.0)	2	24	165	PP	85
78	100 heptene-1	0	0	63	1	SP	0
79	100 heptene-1	Sandoray 1000(1.0)	2	48	3	SM	34
80	100 heptene-1	XL353 (0.15)	2	43	39	PP	73

TABLE III (continued)

Ex. #	Monomers ^(a) (wt. ratio)	Photoinitiator ^(a) (Conc.)/(Wt.%)	No. Passes	Peel Adh. (N/dm)	Shear (Min.)	MOF ^(c)	Gel (%)
81	95 heptene-1, 50D	0	0	38	2	SP	5
82	95 heptene-1, 50D	Sandoray 1000(1.0)	2	32	30	PP	86
83	100 octene-1	0	0	33	1	SP	0
84	100 octene-1	ITX (1.0)	2	24	1	r	74
85	100 octene-1	Sandoray 1000(1.0)	2	21	7	r	90
86	100 octene-1	XL353 (0.15)	2	28	3	r	85
87	98 O-20D	0	0	16	1	SP	0
88	98 O-20D	ITX (0.5)	4	13	1	PP	89
89	95 O-50D	0	0	16	5	SP	9
90	95 O-50D	ITX (1.0)	4	11	13	PP	92
91	98 O-2VCH	0	0	24	2	SP	0
92	98 O-2VCH	ITX (1.0)	4	21	37	PP	82
93	95 O-5VCH	0	0	20	9	SP	0
94	95 O-5VCH	ITX (1.0)	4	15	12	PP	78
95	95 O-5VCH	Sandoray 1000(1.0)	4	15	24	PP	86

TABLE III (continued)

Ex. #	Monomers ^(a) (wt. ratio)	Photoinitiator ^(a) (Conc.)(Wt.%)	No. Passes	Peel Adh. (N/dm)	Shear (Min.)	MOP ^(c)	Gel (%)
96	100 nonene-1	0	0	21	1	SM	17
97	100 nonene-1	Sandoray 1000(1.0)	2	11	2	PP	79
98	100 nonene-1	Sandoray 1000(6.0)	2	4	1	r	74
99	100 nonene-1	XL353 (0.15)	2	23	3	PP	89

^(c)MOP: mode of failure

SM: smear

SP: split

PP: pop off

r: residue

^(a)OD: 1,7-octadiene

VCH: 4-vinylcyclohex-1-ene

ENB: ethylidene norbornene

O: 1-octene

^(a)XL 353: 2,4-bis(trichloromethyl)-6-(3',4'-dimethoxyphenyl)-sym-triazine

ITX: 2-isopropylthioxanthone

5 Examples 100-145 - UV Cured Polyolefin Adhesive Tapes Using Various Photoinitiators and Tackifying Resins

Adhesive solutions of the indicated copolymers, photoinitiators, and tackifying resins in toluene solvent were knife coated on 25 micrometer (μm) PET backing (3M) using a handsread coater (dry coating weights were 3.8 mg/sq cm). The handsreads were dried at 80 °C for 5 minutes to remove the toluene.
 10 The handsreads were cured in nitrogen in an RPC processor Model #QC1202 ANIR (from PPG Industries) at 30 cm/sec (60 ft/min) with two standard medium pressure mercury lamps operating at 80 watts per centimeter. The lamps were located at a distance of about 9.5 cm from the backing. The results for these UV-photocured tapes are shown in Table IV below.

15 Examples 146-181 - E-beam Cured Non-tackified Adhesive Tapes

Adhesive solutions of the indicated copolymers in toluene solvent were knife coated on 25 micrometer PET backing (3M) using a handsread coater (dry coating weights were 3.8 mg/sq cm). The handsreads
 20 were dried at 80 °C for 5 min to remove the toluene. The resulting tapes were E-beam cured using an ElectroCurtain model CB150 (available from Energy Sciences, Inc.) at a web speed of 1.4 m/min and an oxygen concentration of less than 100 ppm. Various dosages of radiation were used to cure the PSAs. The results are shown in Table V below.

25 Examples 182-219 - E-beam Cured Tackified Adhesive Tapes

The indicated copolymers and tackifying resins were dissolved in toluene (15 % solids) to form adhesive coating solutions. The coating, E-beam curing, and test procedures of Example 146-181 were
 30 used to make and test the tapes of these examples. The results are shown in Table VI below.

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TABLE IV

Ex. #	Monomers ^(a) (wt. ratio)	Resin ^(g)	Polymer to Resin ratio	Photoinitiator ^(b) (conc. wt %)	No. of Passes	Peel (N/dm)	Shear (min)	Mode of Failure ^(c)	Gel Failure ^(c) (%)
100	hexene-1	1	75:25	0.5 (ITX)	4	85	35	SP	33
101	98 H-200	1	75:25	0.5 (ITX)	4	90	890	r	31
102	98 H-200	1	75:25	1.0 (ITX)	4	92	317	r	36
103	98H-2VCH	1	90:10	0.25 (ITX)	4	56	18	r	17
104	95H-5VCH	1	75:25	1.0 (ITX)	2	61	1826	r	46
105	95H-5ENB	1	75:25	1.0 (ITX)	4	61	2500	r	52
106	95H-5OD	1	75:25	1.0 (S)	4	63	3900	r	48
107	95H-5OD	1	75:25	1.0 (BP)	4	68	3200	r	41
108	95H-5OD	2	75:25	1.0 (S)	4	79	48	PP	72
109	85H-15OD	3	75:25	1.0 (BP)	4	53	9000+		76
110	95H-5VCH	2	75:25	1.0 (S)	4	73	8500	r	63
111	95H-5VCH	3	75:25	1.0 (S)	4	53	3235	r	69
112	heptene-1	2	95:5	1.0 (S)	2	35	5	SP	60
113	heptene-1	2	50:50	1.0 (S)	2	—	666	SP	50
114	heptene-1	2	95:5	1.0 (XL353)	2	45	26	PP	77
115	95 heptene-1-5OD	2	75:25	1.0 (S)	2	74	1050	r	56
116	95 heptene-1-5OD	3	75:25	1.0 (S)	2	57	940	r	58
117	95 heptene-1-5OD	3	75:25	1.0 (BP)	2	56	625	r	52
118	octene-1	1	75:25	1.0 (ITX)	4	83	7	SP	46

TABLE IV (continued)

Ex. #	Monomers ^(a) (wt. ratio)	Resin ^(g)	Polymer to Resin ratio	Photoinitiator ^(e) (conc. wt %)	No. of Passes	Peel (N/dm)	Shear (min)	Mode of Failure	Gel Failure ^(f) (%)
119	990-10D	1	75:25	1.0 (ITX)	4	50	400	r	63
120	980-20D	1	75:25	1.0 (ITX)	4	53	8000 ⁺		57
121	980-2VCH	1	75:25	1.0 (ITX)	4	79	8	PP	30
122	980-2VCH	1	75:25	1.0 (S)	4	68	45	PP	51
123	950-5VCH	1	85:15	1.0 (ITX)	6	58	29	PP	80
124	octene-1	2	75:25	B(1.0)	4	78	51	SP	62
125	octene-1	2	75:25	ITX (1.0)	4	88	75	SM	52
126	octene-1	2	75:25	(S)	4	80	37	SM	55
127	octene-1	4	75:25	BP (1.0)	4	74	8	SP	9
128	octene-1	4	75:25	ITX (1.0)	4	78	7	SP	6
129	octene-1	4	75:25	(S)	4	74	32	SP	32
130	octene-1	3	75:25	BP (1.0)	4	79	94	SM	57
131	octene-1	3	75:25	ITX (1.0)	4	76	32	SP	27
132	octene-1	3	75:25	S (1.0)	4	78	110	SM	44
133	octene-1	2	75:25	0	0	85	4	SP	2
134	octene-1	4	75:25	0	0	60	5	SP	5
135	octene-1	1	75:25	0	0	76	2	SP	0
136	octene-1	3	75:25	0	0	84	4	SP	0

TABLE IV (continued)

Ex. #	Monomers ^(a) (wt. ratio)	Resin ^(g)	Polymer to Resin ratio	Photoinitiator ^(e) (conc. wt %)	No. of Passes	Peel (N/dm)	Shear (min)	Mode of Failure ^(f)	Gel Failure ^(g) (%)
137	980-20D	2	75:25	BP (1.0)	4	71	481	SM	62
138	980-20D	4	75:25	BP (1.0)	4	58	35	SP	25
139	980-20D	1	75:25	BP (1.0)	4	72	23	SP	15
140	980-20D	3	75:25	BP (1.0)	4	79	545	r	68
141	nonene-1	2	95:5	0	0	31	2	SP	0
142	nonene-1	2	50:50	0	0	AT ^(h)	10000 ⁺		0
143	nonene-1	2	95:5	S (1.0)	2	19	2	r	88
144	nonene-1	2	50:50	S (1.0)	2	AT	10000 ⁺		85
145	nonene-1	2	95:5	XL	2	31	5	PP	89

^(a) SP: split; SM: smear; r: residue; PP: pop off; ^(b) O: 1-octene; H: 1-Hexene; OD: 1,7-octadiene;

VCH: vinylcyclohexene; ^(c) BP: benzophenone; ITX: 2-isopropylthioxanthone; S: Sandoray 1000;

XL-XL353 photocrosslinking agent

^(h) AT-adhesive transfer

^(e) Resin:

- 1 = Wingtack Plus
- 2 = Regalrez 1126
- 3 = Arton P115
- 4 = Piccolyte A115

TABLE V

Ex. #	Monomers ^(a) (wt. ratio)	Dose (Mrad)	Peel (N/dm)	Shear (Min)	Mode of Failure ^(b)	Gel (%)
146	100 hexene-1	0	33	1	SP	
147	100 hexene-1	2	33	88	SP	13
148	100 hexene-1	4	31	122	SP	29
149	100 hexene-1	6	33	117	SP	33
150	100 hexene-1	10	35	173	SP	50
151	100 hexene-1	15	35	124	SP	55
152	99H-10D	2	37	139	SP	52
153	99H-10D	4	33	133	SM	62
154	99H-10D	6	33	53	PP	63
155	99H-10D	10	31	16	PP	74
156	99H-10D	15	30	29	PP	77
157	98H-20D	2	18	3	SM	69
158	98H-20D	4	15	3	SM	79
159	98H-20D	6	10	1	PP	81
160	98H-20D	10	11	1	PP	89
161	98H-20D	15	8	1	PP	91

TABLE V (continued)

Ex. #	Monomers (a) (wt. ratio)	Dose (Mrad)	Peel (N/dm)	Shear (Min)	Mode of Failure (c)	Gel (%)
162	95H-50D	2	22	6	PP	83
163	95H-50D	4	15	89	PP	87
164	95H-50D	6	13	16	PP	86
165	95H-50D	10	10	35	PP	98
166	100 octene-1	0	31	1	SP	0
167	100 octene-1	2	28	10	SP	34
168	100 octene-1	4	28	11	SP	44
169	100 octene-1	6	26	10	SP	51
170	100 octene-1	10	30	15	SP	67
171	100 octene-1	15	23	5	SP	76
172	98O-20D	2	18	3	SM	69
173	98O-20D	4	15	2	SM	79
174	98O-20D	6	10	950	r	80
175	98O-20D	10	11	685	r	89
176	98O-20D	15	8	2	PP	91

TABLE V (continued)

Ex. #	Monomers ^(a) (wt. ratio)	Dose (Mrad)	Peel (N/dm)	Shear (Min)	Mode of Failure ^(f)	Gel (%)
177	50 O-45H-50D	2	21	12	PP	80
178	50 O-45H-50D	4	18	2	PP	86
179	50 O-45H-50D	6	13	4	PP	86
180	50 O-45H-50D	10	11	3	PP	94
181	50 O-45H-50D	15	7	3	PP	95

^(f) SM: smear; SP: split; r: residue; PP: popoff,

^(a) H: hexene; O: octene; OD: 1,7-octadiene

TABLE VI

Ex. #	Monomers ^(a) (wt. ratio)	resin ^(c)	Polymer to resin ratio (wt. %)	Dose (Mrad)	Peel (N/dm)	Shear (min)	Mode of failure ^(d)	Gel (%)
182	octene-1	1	75:25	2	62	3	SP	5
183	octene-1	1	75:25	4	63	3	SP	8
184	octene-1	1	75:25	6	59	4	SP	19
185	octene-1	1	75:25	10	63	19	SP	57
186	octene-1	1	75:25	15	74	31	SP	52
187	980-200	1	75:25	2	62	2	SP	8
188	980-200	1	75:25	4	69	12	SP	21
189	980-200	1	75:25	6	60	49	SP	54
190	980-200	1	75:25	10	59	53	SP	53
191	980-200	1	75:25	15	57	65	PP	63
192	hexene-1	1	75:25	2	70	45	SP	6
193	hexene-1	1	75:25	4	68	25	SP	9
194	hexene-1	1	75:25	6	59	18	SP	8
195	hexene-1	1	75:25	10	66	13	SP	14
196	hexene-1	1	75:25	15	63	18	SP	12
197	hexene-1	2	75:25	4	83	453	SP	62
198	99H-100	1	75:25	2	62	18	SP	3
199	99H-100	1	75:25	4	63	18	SP	3
200	99H-100	1	75:25	6	62	17	SP	2
201	99H-100	1	75:25	10	57	22	SP	17

TABLE VI (continued)

Ex. #	Monomers ^(a) (wt. ratio)	resin ^(c)	Polymer to resin ratio (wt. %)	Dose (Mrad)	Peel (N/dm)	Shear (min)	Mode of failure ^(e)	Gal failure ^(e) (%)
202	98H-100	1	75:25	15	63	31	PP	62
203	98H-200	1	75:25	2	63	55	SP	14
204	98H-200	1	75:25	4	55	186	SP	20
205	98H-200	1	75:25	6	59	178	SP	35
206	98H-200	1	75:25	10	50	479	SP	47
207	98H-200	1	75:25	15	59	934	SP	49
208	98H-200	2	75:25	4	70	2529	SP	74
209	95H-500	1	75:25	2	59	630	SP	58
210	95H-500	1	75:25	4	44	923	SM	64
211	95H-500	1	75:25	6	46	424	SM	67
212	95H-500	1	75:25	10	50	81	PP	75
213	95H-500	1	75:25	15	39	93	PP	77
214	95H-500	2	75:25	4	69	5000+		73
215	50 O-45H-500	1	75:25	2	55	133	SP	46
216	50 O-45H-500	1	75:25	4	54	272	SM	59
217	50 O-45H-500	1	75:25	6	46	195	SM	62
218	50 O-45H-500	1	75:25	10	46	155	SM	75
219	50 O-45H-500	1	75:25	15	46	47	PP	75

(a) SP: split; SM: smear; PP: pop off;

(b) O: 1-octene; H: 1-hexene; OD: 1,7 octadiene;

(c) tackifying resin type

1 = Wingtack Plus 3 = Arton P115

2 = Regalrez 1126 4 = Piccolyte A115

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

Claims

1. A radiation curable poly(α -olefin) pressure-sensitive adhesive composition comprising:

- at least one polymer comprising the reaction product of from 85 to 100 mole percent C_6 to C_{10} α -olefin and 15 to 0 mole percent of one or more polyene monomer;
- an effective amount of a photoactive crosslinking agent.

2. The composition according to claim 1 wherein said:

a) polymer has the formula:



where R₁ is selected from monovalent hydrocarbon groups containing 4 to 8 carbon atoms;

10 R₂ is a monovalent hydrocarbon radical containing one or more ethylenically unsaturated groups selected from the group consisting of:

{CH₂}_nR₃, -Ar-R₃, {CH₂}_nQ-R₃

n = an integer 0 to 14;

R₃ is a C₂ to C₁₀ monovalent hydrocarbon group containing one or more ethylenically unsaturated groups;

15 Ar is a divalent aromatic radical containing 1 or 2 aromatic rings with from 0 - 8 substituents selected from the group consisting of alkyl, aryl, cycloalkyl, alkoxy, and aryloxy containing from 1 - 12 carbon atoms;

Q is a divalent radical selected from the group consisting of



25

where R₄ and R₅ are the same or different C₁ to C₁₀ monovalent hydrocarbon radicals selected from the group consisting of alkyl, cycloalkyl, alkaryl, aryl, alkoxy, aryloxy;

30 x is the mole percent of one or more C₅ - C₁₀ α-olefin monomer(s) the total ranging from 85 - 100 mole percent;

y is the mole percent of one or more polyene monomer(s) the total ranging from 0 - 15 mole percent; with the proviso that x + y = 100 mole percent.

3. The composition according to claims 1 and 2 wherein the polyene monomers are selected from the group consisting of aliphatic dienes, aliphatic trienes, aliphatic tetraenes, aromatic dienes, aromatic trienes, 35 monocyclic dienes, bicyclic dienes, tricyclic dienes, tetracyclic dienes, monocyclic trienes, bicyclic trienes, tricyclic trienes, and tetracyclic trienes.

4. The composition according to claims 1 to 3 wherein said polymer comprises at least one of residual ethylenically unsaturated groups in pendant side chains and residual ethylenically unsaturated groups in the backbone.

40 5. The composition according to claims 1 to 4 wherein said photoactive crosslinking agent is selected from the group consisting of aldehydes, ketones, quinones, thioxanthenes, and s-triazines.

6. The composition according to claims 1 to 5 further comprising a tackifying resin in an amount in the range of more than 0 to 150 parts per hundred parts of the adhesive composition.

45 7. The composition according to claim 6 wherein said tackifying resin is selected from the group consisting of hydrocarbon resins and polyterpene resins.

8. An article comprising the cured or uncured adhesive composition of claims 1 to 7 coated on a substrate or between two substrates.

9. The article according to claim 8 further comprising at least one of a primer layer and a release liner.

50 10. The article according to claims 8 and 9 which is a pressure-sensitive adhesive tape or a transfer adhesive film.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90309761.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claims	CLASSIFICATION OF THE APPLICATION (Int. CLS)
A	EP - A1 - 0 021 693 : (ROHM AND HAAS COMPANY) * Claims 1,2,4,8-10 *	1,3, 6-8	C 09 J 123/18 C 09 J 7/02
A	DERWENT ACCESSION NO. 79-852 72B, Questel Tele- systems (WPI) DERWENT PUBLICATIONS LTD., London * Abstract * & JP-A-54 133 525 (NITTO ELECTRIC) -----	1,3,5, 6	
			TECHNICAL FIELDS SEARCHED (Int. CLS)
			C 09 J B 32 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 18-12-1990	Examiner BÖHM
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

EXAMPLES**Example 1.**

6 An adhesive composition was prepared with the following composition:

- 39.7 wt% E/nBA, (32.6 wt% nBA, MI = 34)
- 36.7 wt% 'Foral' 85 (Rosin ester Tackifier)
- 10.9 wt% 'Picco' AP-10 (Aromatic hydrocarbon Tackifier)
- 11.9 wt% 'Sunthene' 4240 (Naphthenic Oil Plasticizer)
- 10 0.8 wt% 'Irganox' 1098 (Antioxidant).

Adhesion tests gave the following values: Polyken tack 1518g., SAFT 62° C., and 180 deg. peel adhesion of 1.8 lb./in. As a reference point, a commercially formulated adhesive based on a 'Kraton', indicated to be for the so-called 'mid-performance' market, was subjected to the same tests to give the following results: Polyken Tack 1600g. SAFT 63° C. and 180 deg. peel 3.5 lb./in. The adhesive properties of the E/nBA copolymer adhesive composition were generally comparable except for a lower 180 deg. peel strength.

Example 2

20 In this example a mixture of E/nBA copolymers was used, consisting of 80 wt.% of a copolymer with 40 wt.% nBA, and an MI of 30 and 20 wt.% of a copolymer with 24 wt.% nBA and an MI of 6. The average nBA content was thus 36.8 wt.%. The copolymer component formed 39.7 wt % of the adhesive composition as in Example 1, and all other ingredients and amounts were the same as in Example 1. Properties were as follows: Polyken Tack 1404g., SAFT 60° C. and 180 deg. peel 2.6 lb./in. Here peel was improved compared with example 1.

Example 3

25 This composition was made using the same amount of the same polymer of example 1. All other ingredients were the same except that a higher softening tackifier, 'Foral' 105 was used instead of 'Foral' 85. Properties were as follows: Polyken Tack 850g., SAFT 62° C., and 180 deg. peel 3.75 lb./in. Changing tackifier resulted in improved peel at the expense of some reduction in tack.

Example 4.

35 In this example the E/nBA used had an nBA content of 35.5 and an MI of 15. The amount of this polymeric component and all other components and amounts were identical to those in Example 3. The composition had the following properties: Polyken tack, 1170g., SAFT 61° C., and 180 deg. peel 2.5 lb./in. This example shows that by increasing nBA level a little, the balance of tack and peel is changed somewhat in favor of tack.

Example 5.

40 In this example, the E/nBA used also had an nBA content of 35.5, but had an MI of 30. All other components and amounts were the same as in Example 3 and 4. Properties were: Polyken Tack 1429g., SAFT 58.5° C., and 180 deg. peel of 2.2 lb./in. This shows the effect of melt index. In a comparable composition, as melt index increases the SAFT decreases.

45 By way of comparison, a composition was made which shows the effect of very low melt index (high viscosity). The copolymer component consisted of a blend of 80 wt.% of an E/nBA resin with 40 wt.% nBA and an MI of 1.98 and 20 wt.% of an E/nBA resin with 24 wt.% nBA and an MI of 6. Average nBA content is 36.8 wt.%. MI of the blend was less than 5. All other ingredients and amounts were the same as in Example 3, 4 and 5. Properties were: Polyken Tack 280g., SAFT 69° C., and 180 deg. peel 1.8 lb./in. This shows that when the MI is too low, tack suffers drastically, though SAFT increases. This may be compared with Example 5, where high MI reduced SAFT.

Example 6.

55 This example shows the effect of increasing the nBA to 40 wt. % in the copolymer. The copolymer used was an E/nBA with 40 wt.% nBA and an MI of 15. All other components and amounts were the same as in Examples 3, 4 and 5. Properties were: Polyken Tack 1012g., SAFT 51.3° C. and 180 deg. peel 2.3 lb./in. As the nBA

is increased, corresponding to a reduction in the crystallinity level of the copolymer, SAFT is drastically reduced. At this high level of nBA, adjustment in MI and/or a different formulation would be necessary to obtain a more desirable combination of adhesive properties.

6 Example 7.

This example shows the effect of decreasing nBA level to 30 wt. % of the copolymer. The polymer used had only 30 wt.% nBA and the MI was 15 as in comparative Example 2. All other components and amounts were the same as in Examples 3,4 and 5. Properties were as follows: Polyken Tack 379g., SAFT 61° C., and
10 180 deg. peel 1.3 lb./in. As the nBA is decreased to the lower acceptable level, corresponding to a stiffer more crystalline resin, this particular formulation gave a low value for tack and 180 deg. peel. Very careful formulation would be necessary to achieve more desirable properties at this low nBA level.

15 Example 8.

In this example, no 'plasticizer' was used, but a liquid rosin ester tackifier was included in the blend. While this tackifier is not commonly referred to as a plasticizer, some liquid tackifiers appear to serve a similar function. The copolymer component consisted of 80 wt.% of an E/nBA resin with 40 wt.% nBA and an MI of 30 and 20 wt. % of an E/nBA with 24 wt.% nBA and an MI of 6, the copolymer component being 31.9 wt.% of the adhesive
20 composition, 36.8 wt.% 'Permalyne' 85 a rosin ester tackifier, 22.9 wt. % 'Herculyn' D, a liquid rosin ester tackifier and 0.5 wt.% of 'Irganox' 1098 antioxidant. Properties were as follows: Polyken Tack 972g., SAFT 60° C., and 180 deg. peel 1.6 lb./in. While these properties are not as good as in some other examples, they nevertheless are considered acceptable.

25 Examples 9,10 and 11.

In these examples, a mixture of copolymers containing methacrylic acid was used as the polymer component. The polymer mix consisted of 85 wt.% of an E/nBA/MAA polymer containing 40 wt.% nBA and 3 wt.% MAA with an MI of 35 and 15 wt.% of a copolymer containing 24 wt.% nBA and 3 wt.% MAA with an MI of 12.
30 Average nBA content of the mix was thus 37.6 wt.%. In Example 9 the polymer was used as is. In example 10, 13.1 % of the methacrylic acid groups were neutralized with zinc ions and in Example 11, 26.1 % of the acid was neutralized with zinc ions. In all three examples the polymer component formed 39.7 wt.% of the composition, and all other components and amounts were the same as in Example 3. Properties were as follows:

35		<u>Polyken Tack.g.</u>	<u>SAFT °C.</u>	<u>180 deg. peel.</u>
	Ex. 9	1170	61	3.5
	Ex. 10	1128	64	2.5
40	Ex. 11	1120	68	2.3

It can be seen that as the level of neutralization increases, the SAFT increases, but 180 deg. peel, though quite acceptable starts to drop.

45 Example 12.

This example is similar to Example 1 except that the rosin ester tackifier used was 'Stabylite' Ester 10 instead of 'Foral' 85, and the plasticizer was 'Santicizer' 261 (octyl benzyl phthalate) instead of 'Sunthene' naphthenic oil. All quantities were the same. Polyken Tack was 688g. and SAFT was 56° C. Peel was not
50 measured. While properties would still be acceptable for some uses, the phthalate plasticizer gives poorer tack in this particular formulation.

'Foral' tackifiers are manufactured by Hercules Inc.

'Picco' tackifiers are manufactured by Hercules Inc.

'Stabylite' tackifiers are manufactured by Hercules, Inc.

55 'Santicizer' plasticizers are manufactured by Monsanto, Inc.

'Sunthene' plasticizers are manufactured by Sun Oil Co.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except

as defined in the appended Claims.

Claims

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1. A hot melt pressure sensitive adhesive composition consisting essentially of (a) about 25 to 50% by wt. of copolymer having a melt index of about 5 to 40 g/10 min. of (i) about 60 to 70% by wt. of ethylene, (ii) about 30 to 40% by wt. of n-butyl acrylate, and (iii) 0 to about 5% by wt. of (meth)acrylic acid, based on the weight of the copolymer, with the acid being 0 to about 40% neutralized by metal ions and (b) tackifier and optionally, plasticizer, in an effective amount from about 50 to 75% by wt. based on the total weight of the composition whereby said composition is a pressure sensitive adhesive.
2. The adhesive composition of Claim 1 wherein the amount of said acid is about 0.5 to 5% by wt.
- 15 3. The adhesive composition of Claim 1 or Claim 2 wherein said acid is methacrylic acid.
4. The adhesive composition of Claim 1, 2 or 3 wherein about 25 to 65% by wt. of said tackifier is present in the composition and about 5 to 25% by wt. of said plasticizer is present in the composition.
- 20 5. The adhesive composition of any one of Claims 1 to 4 exhibiting a shear adhesion failure temperature of at least 55°C.
6. The adhesive composition of any one of Claims 1 to 5 wherein said tackifier is selected from the group consisting of rosin acids derived from wood, gum or tall oil and their hydrogenated, disproportionated, mildly polymerized or ester derivatives; terpene resins; dicyclopentadiene-aromatic hydrocarbon resins; and low molecular weight styrene or substituted styrene resins.
- 25 7. The adhesive composition of Claim 6 wherein said tackifier is rosin ester.
- 30 8. The adhesive composition of any one of Claims 1 to 7 wherein said plasticizer is selected from the group consisting of phthalates, azelates, adipates, tricresyl phosphate, polyesters, and low molecular weight alkylated phenol, phenol modified Coumarone-indene, terpene and synthetic terpene resins, and processing oils.
- 35 9. The adhesive composition of Claim 8 wherein said plasticizer is naphthenic processing oil.

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